

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 693 508 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:

24.01.1996 Bulletin 1996/04

(51) Int. Cl.⁶: **C08F 220/56**, **C08F 220/06**,
C08L 33/26

(21) Application number: **95907867.6**

(86) International application number: **PCT/JP95/00183**

(22) Date of filing: **10.02.1995**

(87) International publication number: **WO 95/21876**
(17.08.1995 Gazette 1995/35)

(84) Designated Contracting States:

AT BE CH DE ES FR GB GR IT LI NL PT

(30) Priority: **10.02.1994 JP 36387/94**

28.09.1994 JP 257349/94

(71) Applicant: **KOHJIN CO. Ltd.**

Minato-ku Tokyo 105 (JP)

(72) Inventors:

• **MURAYAMA, Teiichi**
Kumamoto 866 (JP)

• **MARUYAMA, Takashi**
Kumamoto 866 (JP)

(74) Representative: **Hansen, Bernd, Dr. Dipl.-Chem. et al**

D-81925 München (DE)

(54) TEMPERATURE-SENSITIVE WATER-ABSORBING/DESORBING POLYMER COMPOSITION

(57) A temperature-sensitive water-absorbing/desorbing polymer composition having a temperature-sensing point fit to a target temperature and produced by the aqueous solution polymerization of N-isopropylacrylamide and/or N,N-diethylacrylamide, acrylic acid and/or alkali metal acrylate, and diacetoneacrylamide and/or acrylamide in the presence of a cross-linking agent. The composition has an arbitrarily adjustable temperature-sensing point and a high water-absorbing/desorbing capacity in the vicinity of the temperature-sensing point. Hence it can be applied to a wide variety of fields including sanitary materials such as paper diaper, soil conditioners in the agrohorticultural fields of plants and vegetables such as soil water supplying and refilling materials, waterproofing sealing material, sandbags, temperature sensor, chemical pulp, solid-liquid separation, and condensing materials.

EP 0 693 508 A1

Description

Technical Field

5 The present invention concerns a novel water absorbing resin having water absorbability that changes greatly at a certain temperature near a room temperature as a boundary and repeating water absorption and discharging in accordance with the temperature.

Background Art

10

A water absorbing resin has been used in various application uses, for example, as sanitary materials such as menstrual articles, diapers and disposable napkins or as water retaining agent in agricultural or horticultural uses or condensation prevention in building materials. As such a water absorbing resin, hydrogels using carboxymethyl cellulose crosslinking products, starch - acrylonitrile graft copolymers, polyvinyl alcohols and polyacrylates as the raw materials
15 have been generally known. However, such hydrogels mentioned above have only one function of starting water absorption upon contact with water.

However, it has been attempted in recent years to further add other functions. For instance, as shown in Japanese Patent Laid-Open sho 61-55180, a non-ionic hydrogel having a function of reversibly repeating water absorption and discharging depending on the change of temperature has been known. That is, the hydrogel scarcely shows water
20 absorption if a water temperature is higher than a certain temperature and can absorb water if the temperature lowers to less than the certain temperature. However, since the hydrogel is non-ionic, it has small water absorbing amount at a low temperature and it is not practical. For increasing the water absorbing amount, it has been reported a copolymerized hydrogel of n-isopropyl acrylamide and an ionic monomer such as a sodium acrylate, for example, in USP No. 4,732,930 and J. Chem. Phys. 1987, 87, 1392.

However, although the hydrogel with the ionic monomer described above is improved for the water absorbing amount, it involves a drawback that the inherent temperature sensing point (a boundary temperature that water absorbability
25 exits lower than the temperature but is almost lost at a higher temperature) changes greatly by merely copolymerizing the ionic monomer slightly, more specifically, a drawback that the temperature sensing point rises as the content of the ionic monomer is increased making it difficult to obtain a composition showing a temperature sensitivity near the room
30 temperature.

Further, various methods have been proposed for improving the water absorbing characteristic of a gel having a sensitive and reversible water absorbing and discharging performance relative to the change of temperature in water. For instance, there have been known, for example, a method of an mixing iron oxide in an aqueous solution of polyvinyl methyl ether, irradiating γ -rays, thereby improving porosity and heat transfer rate to improve the water absorbing rate (J.
35 Chem. Eng. Japan, 21, 10, 1988), a method of previously mixing hydroxyl propyl cellulose upon synthesis of a gel, cleaning the gel after polymerization to remove hydroxypropyl cellulose, thereby making the gel porous to improve the water absorbing rate (J. Polym. Soc.: Part A, 30, 2121, 1992) and a method of synthesizing a gel having not homogeneous crosslinking structure by polymerization at a temperature higher than a volume transition temperature (polymer communications, 32, 322, 1991). On the other hand, various improvements for water absorbing characteristic have also been
40 conducted on general highly absorbing resins having no water absorbing and discharging performance relative to the change of the temperature. For instance, there have been reported, for example, a method of mixing a water absorbing resin powder with hydrotalcite to improve the water absorbing rate (Japanese Patent Laid-Open Hei 2-215863), and a method of mixing a water absorbing resin powder with attapulgite to improve the water absorbing rate (Japanese Patent Laid-Open Sho 61-58657).

However, although the methods can improve the water absorbing rate, they involve problems in that the production
45 process for the gel is extremely complicate or the water absorbing rate of the resultant gel is not sufficient.

Disclosure of the Invention

50 The present inventors, et al have made earnest studies for obtaining a resin free from the foregoing drawbacks and, as a result, have found that when N-alkyl acrylamide derivative and acrylic acid or alkali metal salt of acrylic acid are copolymerized in an aqueous solution, a temperature sensitive hydrogel maintaining high water absorbing and discharging property can be obtained by introducing diacetone acrylamide and/or acrylamide, the temperature sensitive point can be adjusted within a wide range in a lower temperature region by changing the amount of diacetone acrylamide to
55 be introduced and, therefore, the temperature sensitive point depending on the aimed temperature can be set easily, to complete the present invention.

That is, the present invention provides a temperature sensitive water absorbing and discharging polymer composition obtained by copolymerizing an aqueous solution containing N-isopropyl acrylamide and/or N,N-diethyl acrylamide,

acrylic acid and/or alkali metal salt of acrylic acid and diacetone acrylamide and/or acrylamide under the presence of a crosslinking agent.

The blending amount of the N-isopropyl acrylamide and/or N,N-diethyl acrylamide is desirably from more than 30 mol%, more preferably, more than 50 mol% of the entire monomer used in view of the temperature sensitivity although it depends on the amount of other monomers used.

Further, as the acrylic acid and/or acrylate, acrylic acid and/or alkali metal salt of acrylic acid is preferred. As the alkali metal salt of acrylic acid, there can be mentioned, for example, alkali acrylate such as sodium acrylate, potassium acrylate, calcium acrylate and magnesium acrylate or ammonium acrylate, sodium acrylate being particularly preferred. The amount of the acrylic acid and/or acrylic acid salt used, although depending on the kind thereof, is from 0.5 to 40 mol%, more preferably, 1 to 12 mol% based on the total amount of the acrylamide derivative and/or N,N-diethyl acrylamide, diacetone acrylamide and/or acrylamide.

Since diacetone acrylamide and/or acrylamide is freely soluble to water, it can be used in a wide range of amount and it is desirably from 0.1 to 40 mol% of the entire amount of the monomer to be used, in view of the temperature sensitivity. If it is less than 0.1 mol%, no substantial effect can be obtained.

Further, as a method of producing a temperature sensitive water absorbing and discharging polymer composition having a crosslinked structure by polymerizing an aqueous monomer solution as described above, there can be mentioned, for example, a method of copolymerizing a divinyl type monomer, a method of copolymerizing a crosslinkable vinyl monomer and then crosslinking the same by a crosslinker or a method of crosslinking by radioactive rays, the method of copolymerizing the divinyl type monomer being more preferred since the production process is convenient.

As the divinyl type monomer used, a monomer having good copolymerizability with each of the monomers constituting the temperature sensitive polymer, capable of efficiently taking a crosslinked structure and providing uniform crosslinking distribution is preferred and there can be mentioned, for example, N,N-methylenebis(meth)acrylamide, ethylene glycoldi(meth)acrylate, diethylene glycol(meth)acrylate, polyethylene glycoldi(meth)acrylate, propylene glycoldi(meth)acrylate and glycerine tri(meth)acrylate. The amount of the divinyl monomer to be used is about 0.001 to 5 wt% and, preferably, about 0.01 to 1 wt% based on the entire monomer.

Further, the inventors of the present application have found that a temperature sensitive water absorbing and discharging composition sensitive to the change of temperature and excellent in water absorbing and discharging rate, is obtained by conducting aqueous solution polymerization under the presence of inorganic particles.

The inorganic particles to be present are optional and one or more of materials selected preferably from acidic white clay, diatomaceous earth and kaolin are preferred.

Referring to the amount of the inorganic particles used, they are added by 2 to 50 parts by weight, preferably, 5 to 20 parts by weight based on 100 parts by weight of the polymer forming ingredients. If they are added in excess of 50 parts by weight, the water absorbing amount of the resultant temperature sensitive water absorbing and discharging composition is lowered, whereas if it is less than 2 parts by weight, no sufficient improvement can be obtained for the water absorbing and discharging rate. The inorganic particles used here preferably have a particle size from 0.001 to 100 μm . If it is greater than 100 μm , dispersibility upon polymerization is worsened, wherein if it is less than 0.001 μm , there is a problem that no sufficient improvement can be expected for the water absorbing characteristic.

A process for producing the polymer composition according to the present invention is practiced by dissolving each of monomers constituting the temperature sensitive polymer and a divinyl type monomer added as required into a solvent, adding to the solution inorganic particles to be present optionally, mixing and dispersing them and then polymerizing under the presence of a catalyst. There is no particular restriction for the solvent usable herein so long as it dissolves the monomers and use of water as a solvent is preferred in view of the production efficiency and safety. Further, if the inorganic fine particles are added and mixed after polymerization or after drying and pulverization of the polymer, uniform dispersion of the organic particles is difficult or inorganic particles are lost and, accordingly, no sufficient improvement can be expected for the water absorbing rate.

As a process for producing the polymer composition according to the present invention, aqueous solution polymerization is essential but any of methods known generally in the aqueous solution polymerization can be used. A polymerization initiator used in this case is a water soluble radical polymerization initiator, for example, hydrogen peroxide or persulfate such as ammonium persulfate or potassium persulfate, hydroperoxides such as t-butyl hydroperoxide or cumene hydroperoxide, azo type initiator such as 2,2'-azobis(2-amidinopropane) dihydrogen chloride, or such water soluble initiator may be combined with, for example, a reducing substance such as sodium hydrogen sulfite or amines such as N,N,N',N'-tetramethylethylenediamine and used as a redox type initiator. The amount of the water soluble radical polymerization initiator used is from 0.01 to 10 wt% and, preferably, from 0.1 to 2 wt%.

Best Mode for Practicing the Invention

The present invention will be explained more specifically with reference to examples.
Evaluation for the present invention will be measured by the following method.

(1) Water Absorbing Rate

After sealing 0.2 g of a temperature sensitive water absorbing and discharging composition in a non-woven fabric bag, and immersing it in purified water controlled to a temperature of 10°C for 10 min, it was sufficiently drained and weighed. Separately, a non-woven fabric bag not containing the composition was treated in the same manner and it was used as a blank. A blank was subtracted from the resultant measured value, and a value converted into the weight per 1 g of the dry composition was defined as the water absorbing rate. As the value is larger, the water absorbing rate is greater.

(2) Water Discharging Rate

After sealing 0.2 g of a temperature sensitive water absorbing and discharging composition in a non-woven fabric bag and immersing it in purified water controlled to a temperature of 10°C for 15 hours, sufficiently causing water to be absorbed, it was placed in purified water controlled to a temperature of 50°C, water was drained from the composition and a time till complete draining (time reaching a constant weight) was measured, and the time was defined as a water discharging rate. As the value is smaller, the discharging rate is greater.

(3) Water Absorbing Amount

After sealing 0.2 g of the temperature sensitive water absorbing and discharging composition into a non-woven fabric bag, and immersing it in purified water controlled to an optional temperature for one day, it was sufficiently drained and then weighed. Separately, a non-woven fabric bag not containing the composition was treated in the same manner and used as a blank. The blank was subtracted from the obtained measured value and a value converted into weight per 1 g of the dry composition was defined as a water absorbing amount at each temperature. As the value is greater, it has higher water absorbability.

Example 1

In a 500 ml separable flask, were added 17.82 g of N-isopropyl acrylamide, 1.48 g of an aqueous 40% aqueous solution of sodium acrylate, 8.88 g of diacetone acrylamide, 0.1 g of N,N-methylenebis acrylamide and 150 ml of purified water. Then, in a nitrogen atmosphere, 0.24 g of ammonium persulfate and 0.30 ml of N,N,N',N'-tetramethylethylene diamine were added at 10°C to start polymerization. After the copolymerization was over, it was warmed and a gel was taken out and dried in an electric drier at 100°C. The dried gel (resin) was pulverized and the water absorbing factor was measured. The resultant water absorbing factor is shown in Table 1.

Example 2

The procedures were the same as those in Example 1 except for using 20.03 g of N,N-diethyl acrylamide instead of N-isopropyl acrylamide in Example 1 to obtain a resin. The water absorbing factor of the resultant resin is shown in Table 1.

Comparative Example 1

A resin was obtained by the same procedures as those in Example 1 except for not using diacetone acrylamide and sodium acrylate and replacing them with 23.76 g of N-isopropyl acrylamide in Example 1. The water absorbing factor of the resultant resin is shown in Table 1.

Comparative Example 2

A resin was obtained by the same procedures as those in Example 2 except for not using diacetone acrylamide and sodium acrylate and replacing them with 26.71 g of N,N-diethyl acrylamide in Example 2. The water absorbing factor of the resultant resin is shown in Table 1.

Comparative Example 3

A resin was obtained by the same procedures as those in Example 1 except for not using diacetone acrylamide and replacing it with 23.76 g of N-isopropyl acrylamide in Example 1. The water absorbing factor of the resultant resin is shown in Table 1.

Comparative Example 4

A resin was obtained by the same procedures as those in Example 1 except for not using diacetone acrylamide and replacing it with 4.52 g of methyl acrylate as a hydrophobic monomer in Example 1. The water absorbing factor of the resultant resin is shown in Table 1.

Comparative Example 5

A resin was obtained by the same procedures as those in Example 1 except for not using diacetone acrylamide and replacing it with 6.73 g of n-butyl acrylate as a hydrophobic monomer in Example 1. The resultant resin was not uniform.
 5 Since the resin in this case was not uniform, measurement for the water absorbing factor was not conducted.

Comparative Example 6

A resin was obtained by the same procedures as those in Example 1 except for not using diacetone acrylamide and
 10 replacing it with 4.47 g of methacrylamide as a water soluble monomer in Example 1. The water absorbing factor of the resultant resin is shown in Table 1.

Example 3

15 A resin was obtained by the same procedures as those in Example 1 except for replacing sodium acrylate with 1.06 g of acrylic acid, ammonium sulfate and N,N,N',N'-tetramethylethylene diamine as the polymerization initiator with 0.027 ml of tert-butylhydroperoxide and 0.033 g of LONGARIT (WaKo Junyaku) respectively. The water absorbing factor of the resultant resin is shown in Table 1.

20 Comparative Example 7

A resin was obtained by the same procedures as those in Example 1 except for not using diacetone acrylamide and replacing it with 23.76 g of N-isopropyl acrylamide in Example 3. The water absorbing factor of the resultant resin is
 25 shown in Table 1.

Comparative Example 8

A resin was obtained by the same procedures as those in Example 3 except for not using diacetone acrylamide and
 30 replating the amount of methyl acrylate as a hydrophobic monomer into 4.52 g in Example 3. The water absorbing factor of the resultant resin is shown in Table 1.

Table 1

Gel used	Temperature (°C)				
	10	20	30	40	50
Example 1	247	224	57	12	3
Example 2	186	128	23	7	3
Comp. Example 1	41	36	25	3	-
40 Comp. Example 2	29	22	5	4	-
Comp. Example 3	251	247	240	226	226
Comp. Example 4	266	260	250	199	52
45 Comp. Example 6	230	226	220	207	193
Example 3	142	134	9	2	-
Comp. Example 7	150	141	130	15	2
50 Comp. Example 8	142	125	100	13	3

As apparent from Table 1, the resins according to the present invention maintain higher water absorbability and temperature sensitive property as compared with other resins.

Examples 4 - 8

Resins were obtained quite in the same procedures as those in Example 1 except for using combinations of the amounts of monomers described in Table 2. The water absorbing factors of the resultant resins are shown in Table 3.

Table 2

Example	N-isopropyl acrylamide (g)	Diacetone acrylamide (g)
4	16.63	10.66
5	19.01	7.11
6	20.20	5.33
7	21.39	3.55
8	22.58	1.78

Table 3

Gel used	Temperature (°C)				
	10	20	30	40	50
Example 4	200	162	40	9	3
Example 5	227	216	141	27	5
Example 6	235	224	170	63	12
Example 7	228	208	185	96	14
Example 8	224	214	194	154	33

Examples 9 - 12

Resins were obtained quite in the same procedures as those in Example 3 except for using combinations of the amounts of monomers described in Table 4 and changing the amount of acrylic acid to 0.47 g. The water absorbing factors of the resultant resins are shown in Table 5.

Table 4

Example	N-isopropyl acrylamide (g)	Diacetone acrylamide (g)
9	19.01	7.11
10	20.20	5.33
11	21.39	3.55
12	22.58	1.78

Table 5

Gel used	Temperature (°C)				
	15	20	25	30	35
Example 9	68	60	3	2	1
Example 10	67	57	24	2	1
Example 11	76	72	55	12	2
Example 12	85	84	77	62	9

As apparent from Tables 3 and 5, the temperature sensitive point can be changed by changing the amount of diacetone acrylamide introduced while maintaining high water absorbability.

Example 13

300 ml of purified water was charged in a 500 ml separable flask and, under stirring, 20.44 g of N-isopropyl acrylamide, 4.97 g of diacetone acrylamide, 1.06 g of acrylic acid, 0.14 g of N,N'-methylenebis acrylamide, 2.66 g of acid white clay (NIKKANITE S-200, manufactured by Nippon Kassei Hakudo Co.) were added, dissolved and dispersed. After cooling under a nitrogen gas stream till the liquid temperature was lowered to the 0°C, 0.099 g of LONGARIT and 0.081 ml of t-butyl hydroperoxide were added to conduct polymerization under heat insulating condition. After the reaction was over, a gel was taken out of the flask, dried at 100°C and then pulverized and classified, to obtain a composition (powder) with a grain size of 150 to 500 μ m.

Water absorbing rate, water charging rate and water absorbing amount were measured for the resultant composition. The results are shown in Table 1.

Examples 14- 23

Compositions were obtained by using monomers, inorganic particles as described in Tables 6 and Table 7, and by the same procedures as those in Example 13. Same evaluation was also conducted to the resultant compositions and the results are shown in Table 6 and Table 7.

(1) Symbols in the tables are as below.

Monomer		Inorganic particles	
NIPAN	N-isopropyl acrylamide	J	Acidic white clay (Nippon Kassei Hakudo)
AAM	Acrylamide	K	kaolinite (Wako Junyaku)
DAAM	Diacetone acrylamide	D	Diatomaceous earth (Wako Junyaku)
AAc	Acrylic acid		
MBAAM	N,N-methylene-bisacrylamide		

(2) Unit for the monomer amount (g)

Unit for the water absorbing amount at each temperature (g/g)

Table 6

Amount of monomer	Example					
	13	14	15	16	17	18
NIPAN			20.44			
AAm						
DAAm			4.97			
AAc			1.06			
MBAAm			0.14			
Inorganic particle						
Kind			J			
Amount (g)	2.66	0.27	1.33	5.32	10.64	15.96
Water absorbing rate (g/g)	50	12	40	47	45	30
Water discharging rate (min)	40					
Water absorbing amount at each temperature						
10°C	120	122	115	122	130	116
15°C	115	118	112	120	125	110
20°C	115	115	110	118	120	105
25°C	110	110	106	115	118	105
30°C	7	6	5	8	6	5
35°C	5	5	5	5	5	5
40°C	5	5	5	5	5	5

Table 7

Amount of monomer		Example					
		13	19	20	21	22	23
	NIPAN	20.44	22.58	20.44	20.44	20.44	22.58
	AAm		0.75				0.75
	DAAm	4.97		4.97	4.97	4.97	
	AAc	1.06	1.82	1.06	1.06	1.06	1.82
	MBAAm	0.14	0.14	0.14	0.14	0.14	0.14
	Inorganic particle						
	Kind	J	J	K	D		
	Amount (g)	2.66	2.44	2.66	2.66		
	Water absorbing rate (g/g)	50	50	45	43	15	12
	Water discharging rate (min)	40				85	
	Water absorbing amount at each temperature						
	10°C	120	125	118	135	122	118
	15°C	115	120	117	132	118	110
	20°C	115	115	110	128	108	105
	25°C	110	113	60	110	105	103
	30°C	7	110	7	10	8	100
	35°C	5	55	5	8	3	50
	40°C	5	5	5	5	3	5

As described above, the feature of the present invention resides in introducing diacetone acrylamide as a water soluble monomer for controlling the temperature sensing point to a lower temperature region optionally in a state of maintaining a high water absorbing factor.

A method of introducing a hydrophobic monomer for controlling the temperature sensing point to a low temperature region has been known. However, since the hydrophobic monomer has a low water solubility, it involves drawbacks, for example, in that polymerization in an aqueous solution is impossible or, even if possible, optional control of the temperature sensing point is impossible since the amount of introduction is limited, and, further, the concentration of the monomer upon polymerization has to be reduced an extremely low concentration. For instance, methyl acrylate known as the hydrophobic monomer has a water solubility of about 6%, and inhomogeneous polymerizate is formed at a concentration higher than that. Further, assuming the water absorbing factor at 10°C as 100 and if the temperature at which the water absorbing factor is reduced to 50 is defined as the temperature sensing point, the temperature sensing point of the polymer is lowered only by 1.7°C in a case of introducing 10 mol% of methyl acrylate as described in Comparative Example 8, whereas the temperature sensing point is lowered extremely as much as by 7°C in the case of diacetone acrylamide as described in Examples 9 - 12. Since diacetone acrylamide used in the present invention is a water soluble monomer and dissolves in water at an optional ratio, a homogeneous resin can be produced easily and the content can be varied optionally. Accordingly, it has an advantage capable of easily setting the temperature sensing point in accordance with on the working temperature while maintaining a high water absorbing factor as it is

Industrial Applicability

As has been explained above, since the temperature sensitive water absorbing and discharging composition according to the present invention can control the temperature sensing point and high water discharging and absorbing property above and below the temperature sensing point, it can be applied to a wide variety of range, for example, sanitary materials such as paper diaper, soil improvers in agricultural and horticultural fields for plants and vegetables, such as

soil water feeding agents or soil water retaining agents, water proof sealing materials, sandbags, temperature sensors, chemical valves, solid-liquid separation and concentrating materials.

Claims

- 5 1. A temperature sensitive water absorbing and discharging polymer composition formed by copolymerizing an aqueous solution containing N-isopropyl acrylamide and/or N,N-diethyl acrylamide, acrylic acid and/or alkali metal salt of acrylic acid, and diacetone acrylamide and/or acrylamide under the presence of a crosslinking agent in an aqueous solution.
- 10 2. A temperature sensitive water absorbing and discharging polymer composition formed by copolymerizing an aqueous solution containing N-isopropyl acrylamide, acrylic acid and diacetone acrylamide under the presence of a crosslinking agent in an aqueous solution.
- 15 3. A temperature sensitive water absorbing and discharging polymer composition formed by copolymerizing an aqueous solution containing N-isopropyl acrylamide, acrylic acid and acrylamide under the presence of a cross-linking agent in an aqueous solution.
- 20 4. A temperature sensitive water absorbing and discharging polymer composition formed by copolymerizing an aqueous solution containing N-isopropyl acrylamide and/or N,N-diethyl acrylamide, acrylic acid and/or alkali metal salt of acrylic acid, and diacetone acrylamide and/or acrylamide under the presence of inorganic particles and a crosslinking agent in an aqueous solution.
- 25 5. A temperature sensitive water absorbing and discharging polymer composition formed by copolymerizing an aqueous solution containing N-isopropyl acrylamide, acrylic acid and diacetone acrylamide under the presence of inorganic particles and a crosslinking agent in an aqueous solution.
- 30 6. A temperature sensitive water absorbing and discharging polymer composition formed by copolymerizing an aqueous solution containing N-isopropyl acrylamide, acrylic acid and acrylamide under the presence of inorganic particles and a crosslinking agent in an aqueous solution.
- 35 7. A temperature sensitive water absorbing and discharging polymer composition as defined in claim 3 or 4, wherein the inorganic particles are one or more of materials selected from acidic white clay, diatomaceous earth and kaolinite.
- 40 8. A process for producing a temperature sensitive water absorbing and discharging polymer composition, which comprises copolymerizing in an aqueous solution N-isopropyl acrylamide and/or N,N-diethyl acrylamide, acrylic acid and/or alkali metal salt of acrylic acid and diacetone acrylamide under the presence of a crosslinking agent, wherein inorganic particles are present.
- 45 9. Utilization of a temperature sensitive water absorbing and discharging polymer composition formed by copolymerizing an aqueous solution containing N-isopropyl acrylamide and/or N,N-diethyl acrylamide, acrylic acid and/or alkali metal salt of acrylic acid, and diacetone acrylamide and/or acrylamide under the presence of a crosslinking agent in an aqueous solution, to sanitary materials such as paper diapers, soil improvers in agricultural and horticultural fields for plants and vegetables such as soil water feeding agents or soil water retaining agents, water proof sealing materials, sandbags, temperature sensors, chemical valves, solid-liquid separation and concentrating materials.
- 50
- 55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP95/00183

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ C08F220/56, C08F220/06, C08L33/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ C08F20/06, C08F220/06, C08F20/56, C08F220/56, C08L33/26

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 61-247716, A (Mitsui Toatsu Chemicals, Inc.), November 5, 1986 (05. 11. 86), Claim (Family: none)	1 - 9
Y	JP, 4-298203, A (Kohjin Co., Ltd.), October 22, 1992 (22. 10. 92), Claim (Family: none)	1 - 9
Y	JP, 4-139206, A (Kohjin Co., Ltd.), May 13, 1992 (13. 05. 92), Claim (Family: none)	1 - 9

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

May 10, 1995 (10. 05. 95)

Date of mailing of the international search report

June 6, 1995 (06. 06. 95)

Name and mailing address of the ISA/

Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.